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# Chemiluminescence measurements of the $N_2^+$ , $N^+ + H_2O$ charge transfer systems at suprathreshold energies: Direct probe of the dynamics of large cross section charge transfer processes

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The state-to-state dynamics of large cross section ion-molecule charge transfer processes at collision energies at which direct mechanisms govern the reaction have been the subject of numerous theoretical<sup>1-5</sup> and experimental<sup>6-11</sup> studies. Large cross sections are generally observed when charge transfer can proceed efficiently at large impact parameters. Since little momentum is transferred in such collisions, near energy resonance exists between the internal energy of the reactants and the products. The probability of transitions to near-resonant energy levels of the products at an intermolecular distance  $R$  and a molecular orientation  $\theta$  is a function of the vibronic coupling  $H_{12,v}(R, \theta)$  between the particular reactant and product states. If this coupling is assumed to be independent of the vibrational coordinate, it may be given by the expression<sup>12</sup>

$$H_{12,v} = H_{12}(R, \theta) \langle v | v' \rangle, \quad (1)$$

where  $H_{12}(R, \theta)$  is the pure electronic coupling and  $\langle v | v' \rangle$  is the Franck-Condon overlap between the vibrational wave functions of the states involved in the ionizing and neutralizing transitions.

Equation (1) integrated in Landau-Zener<sup>12</sup> and Demkov<sup>13</sup> type models has proven to be valuable in reproducing experimentally obtained state-to-state cross sections in the  $(Ar-N_2)^+$  system when using Franck-Condon factors obtained from spectroscopic data of the isolated nitrogen molecule.<sup>4,5,6</sup> We have shown in previous work that such Franck-Condon factors do not necessarily predict the magnitude of resonant charge transfer cross sections accurately.<sup>14</sup> In the case of the  $N^+-CO$  system, for example, energy resonance exists with vibrational states of the product ion that exhibit near-zero Franck-Condon factors, but the charge transfer cross section at suprathreshold energies is nevertheless comparatively large.<sup>14</sup>

We have recently studied the  $N_2^+-H_2O$  (Ref. 15) and the  $N^+-H_2O$  (Ref. 16) charge transfer systems at center-of-mass collision energies ranging from 1 to 15 eV and have found charge transfer to proceed with a very high probability. The  $N_2^+-H_2O$  cross sections are slightly larger than those determined for the  $N^+-H_2O$  system. The product ion time-of-flight measurements demonstrate that in both systems the product  $H_2O^+$  ions are produced with essentially thermal energies in the laboratory frame throughout the measured collision energy range. The charge transfer processes are therefore mainly due to large impact parameter grazing collisions in which little momentum is transferred. Near en-

ergy resonance must therefore exist between the energy levels populated by the reactants and the products of these systems. The exothermicities for the  $N_2^+ + H_2O$  and  $N^+ + H_2O$  charge transfer (2.96 and 1.91 eV, respectively) indicate that population of high vibrational levels of the  $H_2O^+ \tilde{A}^2A_1$  state is in both cases possible. The photoelectron spectrum of  $H_2O$  exhibits significant Franck-Condon factors for bending vibrational levels of the  $\tilde{A}$  state in the energy region given by the exothermicities.<sup>17</sup> Since the  $\tilde{A}-\tilde{X}$  emission has previously been observed in thermal charge transfer between  $Ar^+$  and  $H_2O$  (Ref. 18) and in Penning ionization collisions with water,<sup>19</sup> the presently investigated charge transfer systems represent ideal candidates to study suprathreshold charge transfer processes using chemiluminescence measurement techniques.

Extensive work has been carried out in the field of luminescence measurements from charge transfer<sup>20</sup> and other ion-molecule reactions<sup>21</sup> at suprathreshold collision energies. In that work, the observed emissions are generally the result of small cross section processes due to small impact parameter collisions in which reaction kinetic energy is transferred to internal energy of the products leading to emission. In this communication we report the first measurement of luminescence produced by suprathreshold, large impact parameter, ion-molecule charge transfer collisions in which the excitation energy leading to the emission is solely acquired from the exothermicity of the reaction and not from the translational energy of the collision.

The chemiluminescence measurements are carried out in a modified double mass spectrometer incorporating optical detection. The modifications will be described in detail in a subsequent publication. Briefly, primary ions are produced in a discharge ion source. A mass and energy selected ion beam is generated and passed through a static gas collision cell to which a fiber optic light guide is coupled. The light guide transmits light from the collision volume to a simple Czerny-Turner spectrograph (F/3.7, 0.156 m) equipped with an intensified photodiode array of an optical multi-channel analyzer (OMA, Princeton Instruments, Inc.). The intensified photodiode array is furnished with an S-20 type photocathode. The OMA and spectrograph can be replaced with a photomultiplier and counting electronics to determine total emission rates.

The total emission measurements for the  $(N_2^+ + H_2O)^+$  system exhibit intense emissions with a collision energy dependence that is in qualitative agreement with the charge transfer cross section energy dependence.<sup>15</sup> Figure 1 is a wide spectral range, low resolution (4 nm FWHM) spectrum obtained from  $N_2^+ + H_2O$  collisions at a center-of-mass collision energy of 8.6 eV at which energy the charge

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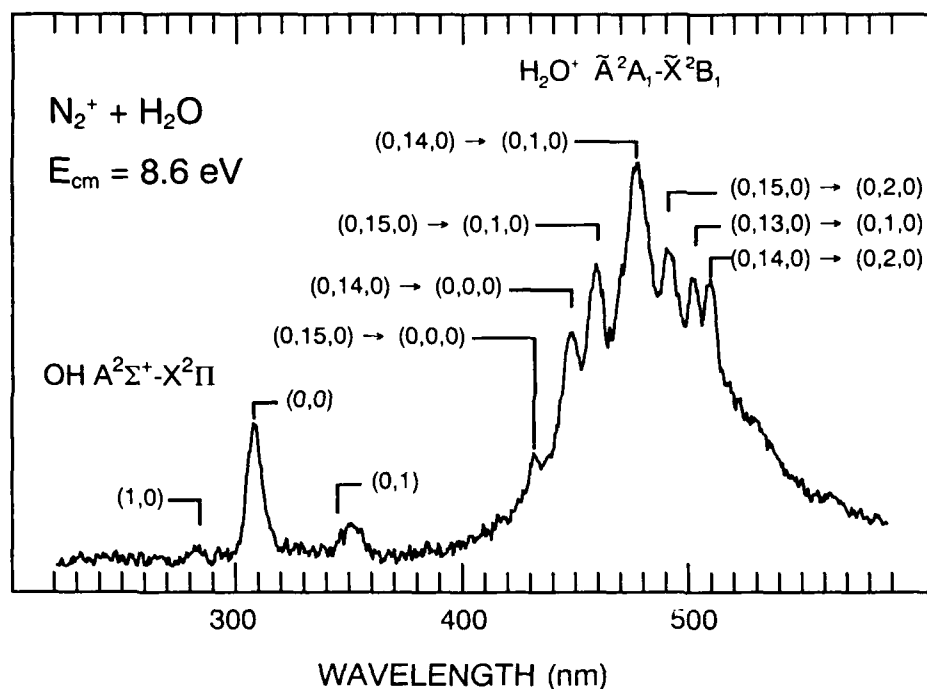


FIG. 1. Emission spectrum obtained from  $N_2^+ + H_2O$  collisions at a collision energy  $E_{cm} = 8.6$  eV. The broad band between 400 and 590 nm is attributed to  $A-X$  emission of  $H_2O^+$ . The wavelengths at the peaks of the observed structure are in good agreement with the indicated  $v_2^-$  bending mode transitions. The spectroscopic data is obtained from Dixon *et al.* (Ref. 17) and Lew (Ref. 22). The band at  $309 \pm 2$  nm is assigned to the  $(0,0)$   $A-X$  transition of OH. The locations of the  $(1,0)$  and  $(0,1)$  bands are also indicated. The band centered at  $352 \pm 2$  nm is tentatively assigned to the  $\Delta v = 1$  sequence of the first negative system of N.

transfer cross section is  $22 \pm 6$  Å<sup>2</sup>.<sup>15</sup> The spectrum is not corrected for the spectral response of the detector. A main band centered at approximately 480 nm is observed that we associate with  $H_2O^+ \tilde{A}^2A_1 - \tilde{X}^2B_1$  emission. The figure also contains a preliminary analysis of the structure observed in the band. The spectroscopic data is obtained from Lew<sup>22</sup> and Dixon *et al.*<sup>17</sup> The analysis indicates that the charge transfer reaction is preferentially populating the bending mode  $v_2^- = 14$  and 15 levels of the  $H_2O^+ \tilde{A}$  state. At the present resolution of the experiment, we do not observe dramatic changes in the shape of the structure of the band when varying the collision energy between 0.8 and 20 eV c.m.

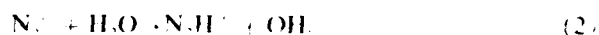
The  $v_2^- = 15$  level of the  $H_2O^+ \tilde{A}$  state is almost resonant with the ground state of  $N_2^+$ . Our results therefore show that essentially all of the exothermicity of the  $N_2^+ + H_2O$  charge transfer is channeled into internal modes of the ionic product. Comparison of the total emission intensity from this system with that obtained from systems where the emission cross section has been determined indicates that this emission cross section is very large, and that a large fraction, possibly all, of the charge transfer collisions produce  $H_2O^+$  in the  $\tilde{A}$  electronic state. This is consonant with Eq. (1) and the fact that the  $v_2^- = 14$  and 15 levels of this state have significant Franck-Condon factors.

The  $N_2^+ + H_2O$  charge transfer, however, exhibits no detectable  $H_2O^+ \tilde{A}$  state emission, despite the fact that this system is energy resonant with  $\tilde{A}$  state vibrational levels that have more favorable Franck-Condon factors than in the  $N_2^+ + H_2O$  system. Consequently, assuming that the nitrogen atom is produced in the ground state, high vibrational levels of the product ion ground electronic state must be populated that have negligibly small Franck-Condon factors. This is in violation of Eq. (1) if the Franck-Condon factors of the

isolated  $H_2O$  molecule are considered to accurately represent the effective overlap. A similar violation has been observed in the  $N_2^+ + CO_2$  charge transfer systems.<sup>11</sup>

A possible explanation for the observed difference in product state population of the presently studied charge transfer systems may be found when correlating the symmetries of the particular reactants and products. If it is postulated that the charge transfer complex maintains  $C_\infty$  symmetry, the totally symmetric  $N_2^+ + H_2O$  charge transfer reactants correlate with the products  $N_2$  and  $H_2O^+$  in their  $X^1\Sigma_g^+$  and  $\tilde{A}^2A_1$  states, respectively. In the  $N_2^+ + H_2O$  charge transfer, the neutralization of the  ${}^2P$   $N^+$  primary ion to a  ${}^1S$  nitrogen atom correlates with the formation of the product  $H_2O^+$  in its  $\tilde{X}^2B_1$  state.<sup>13</sup> Electronic orbital angular momentum conservation has also been suggested as a possible cause of the large difference between the charge transfer cross sections observed in the  $N_2^+ + CO_2$  and  $N_2^+ + CO$  systems.<sup>11</sup>

The spectrum in Fig. 1 also exhibits additional lines in the range 280–400 nm. The main line is centered at  $309 \pm 2$  nm and is identified to be the  $(0,0)$  band of the  $OH \tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$  transition which has a band head at 306.4 nm.<sup>24</sup> The OH is produced in the reaction



This reaction has been shown to proceed via a spectator stripping mechanism.<sup>12</sup> According to this mechanism, the internal energy of the products must increase with collision energy as confirmed by the time-of-flight measurements of the product ions.<sup>12</sup> The 309 nm band appears only at collision energies above 6 eV c.m., in qualitative accordance with the model. An additional peak is observed at  $352 \pm 2$  nm. This band is most likely due to the  $\Delta v = 1$  sequence of the

first negative system of  $N_2^+$  originating from nonreactive inelastic  $N_2^+ - H_2O$  collisions. As indicated in the figure, the peak is also expected to contain contributions from the OH  $A-X(0,1)$  band emissions with band head at 342.8 nm.

We are currently examining the observed band systems with higher resolution. These measurements will provide the product ion vibrational population in the  $N_2^+ + H_2O$  charge transfer. If the resolution and sensitivity permit, information will be obtained regarding the rotational energy of the charge transfer product ions as well as the reaction (2) OH product. The latter would be the first detailed state-to-state analysis of a spectator stripping type process.

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